Features of Potential Signal of Square-wave Voltammetry to Calculate Voltammograms in MATHCAD

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MATHCAD working file is presented for simulation of theoretical voltammograms of a two-step Surface Mechanism coupled with preceding chemical step.

We show the definition and the features of the SWV signa, and how this potential ramp can be calculated in MATHCAD Software.

<u>Legends of the symbols used in MATHCAD File</u>:

potI$_j$ and potII$_j$ are symbols for time-dependent

potential in SWV j and k- are symbols of the

magnitude of potential steps applied r - is a counter

parameter

R - is universal gas constant

x - is symbol for initiation of calculation of the complex equation for current estimation

Δ**E** – is the potential width of

α1 and α2 – are symbols for the electron transfer coefficients of the first and second electron transfer step, respectively

EsI and EsII are the formal redox potentials of the first and the second electron transfer step

KI and KII are the dimensionless rate parameters of the first and the second electrode transformation, respectively;

Esw is the square wave amplitude (50 mV in this file)

dE is potential step (10 mV in this file)

Sk is a numerical integration factor

potIj and potIIj are the formulas for the potential ramp in SWV; they are calculated by a common function by considering the parameters that affect the SWV bias, i.e. the EsI, EsII, Esw and dE.

ΦIj and ΦIIj are the dimensionless potentials of the first and the second electron transfer step

ΨIj and ΨIIj are the total currents of the first and the second electron transfer steps, respectively

Ψnet = ΨIj + ΨIIj is the total current that unifies both electron transfer steps

Meaning of other symbols, and calculating procedure is given in the working file below

TWO STEP SURFACE CEE MECHANISM MATHEMATICAL MODEL IN SQUARE WAVE VOLTAMMETRY

KI and KII are kinetic parameters related to the first and second electron transfer step
alpha is the electron transfer coefficient
EsI and EsII are potentials related to the first and the second electron transfer step
n is number of electron exchanged
F is Faraday constant
Esw is SWV amplitude
T is temperature
dE is potential step
Φ is dimensionless potential
Ψ is dimensionless current
K is equilibrium constant -Keq
z is dimensionless chemical parameter-Kchemical = ε/f

$EsI := 0.2 \quad \Delta E := 0.8 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.6 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{0 \cdot r}$

$KII := 10^0$

$j := 1..\frac{\Delta E}{dE} \cdot 50$

$\alpha 2 := 0.5$

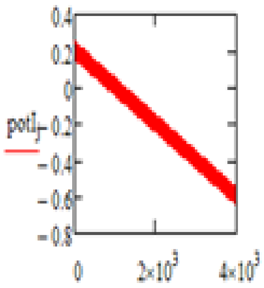
$\alpha 1 := 0.5 \qquad \log(KI_r) = \boxed{0}$

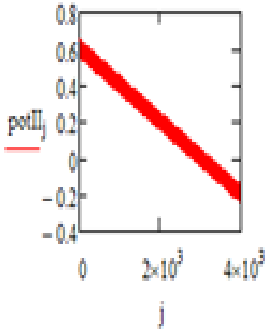
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$$potII_j := EsII + Esw - \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$K := 0.1$

$z := 2$





$k := 1..\frac{\Delta E}{dE} \cdot 50$

$$S_k := e^{\frac{z}{50} \cdot (-k)} - e^{\frac{z}{50} \cdot (-k+1)}$$

$\Phi I_j := n \cdot \frac{F}{R \cdot T} \cdot potI_j \qquad \Phi II_j := n \cdot \frac{F}{R \cdot T} \cdot potII_j$

$x := 0.001$

$$\Psi I_{1,r} := root\left[\left[\frac{\frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot 0\right) - (z)^{-1} \cdot KI_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha 1 \cdot \Phi I_1} \cdot 0 - \frac{KI_r}{50} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot 0}{\frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1} \cdot K}{1+K} \cdot \frac{1}{50} + 1 + (z)^{-1} \cdot KI_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + \frac{KI_r}{50} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)}} \cdot (1+0)\right] x - \frac{KI_r}{50} \cdot e^{(1-\alpha 1) \cdot \Phi I_1} \cdot \left[\frac{x \cdot \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50}}{1 + \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1}\right)}\right] - KI_r \cdot e^{-\alpha 2 \cdot \Phi I_1}, x\right]$$

$$\Psi II_{1,r} := \frac{\Psi I_{1,r} \cdot \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50}}{1 + \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1}\right)}$$

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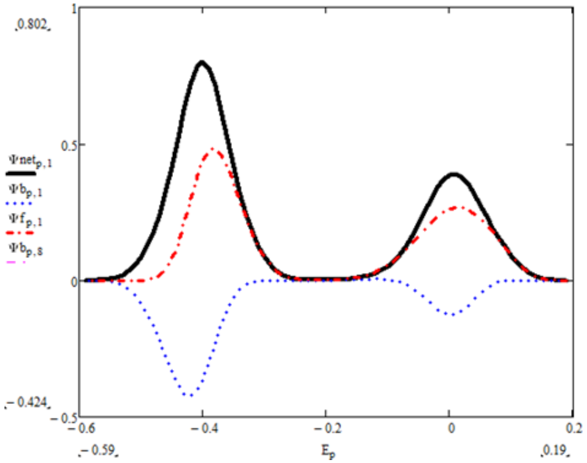
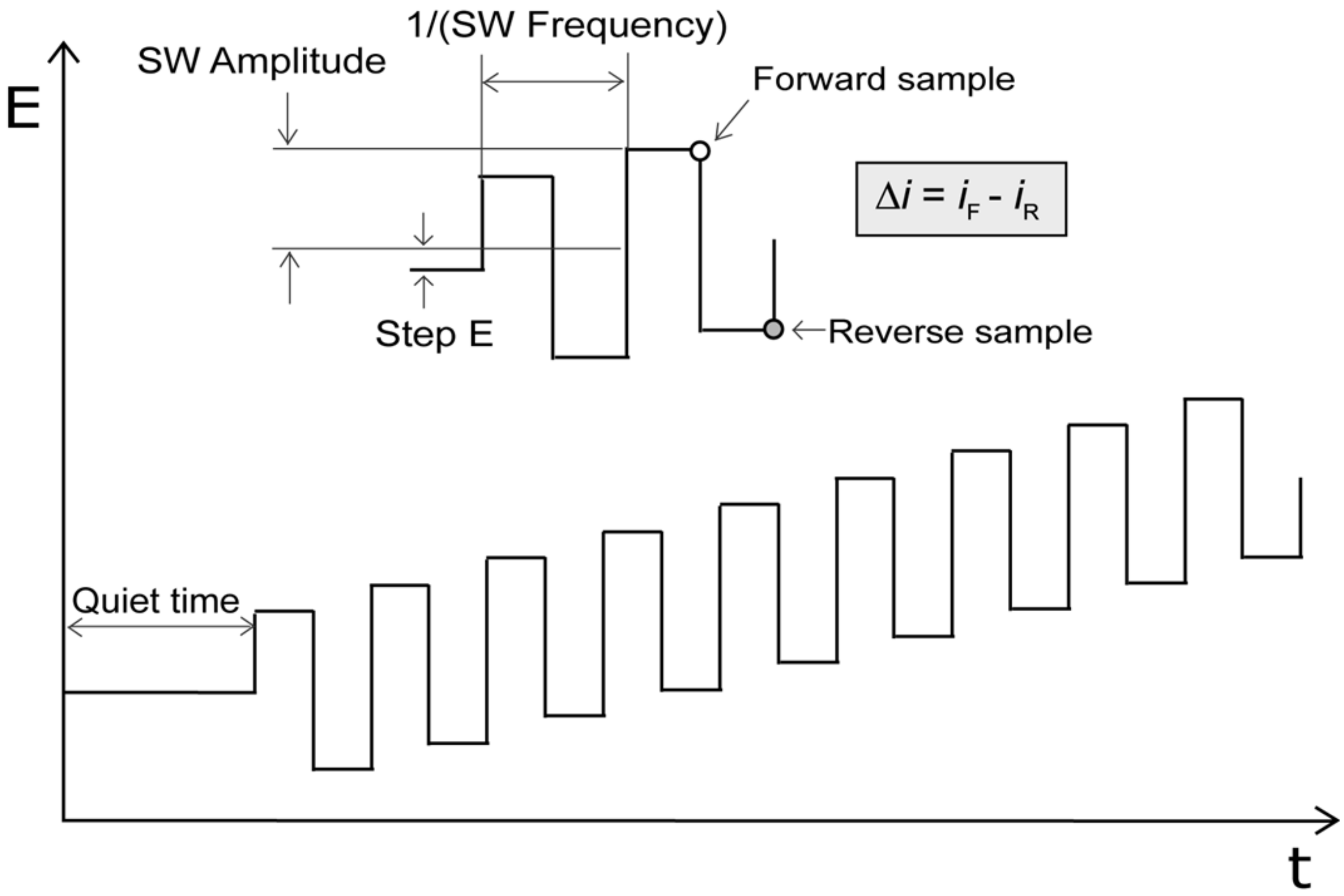
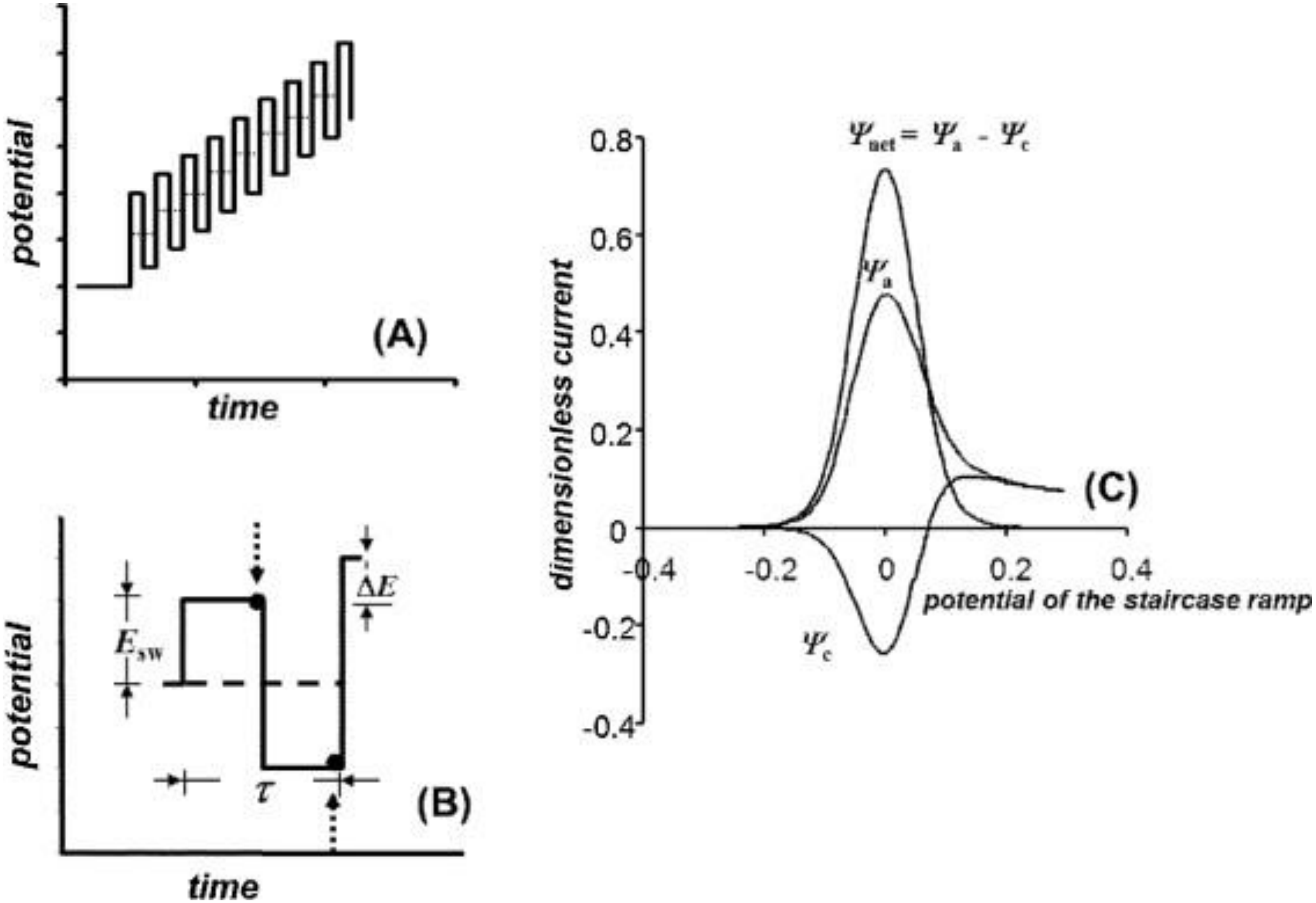
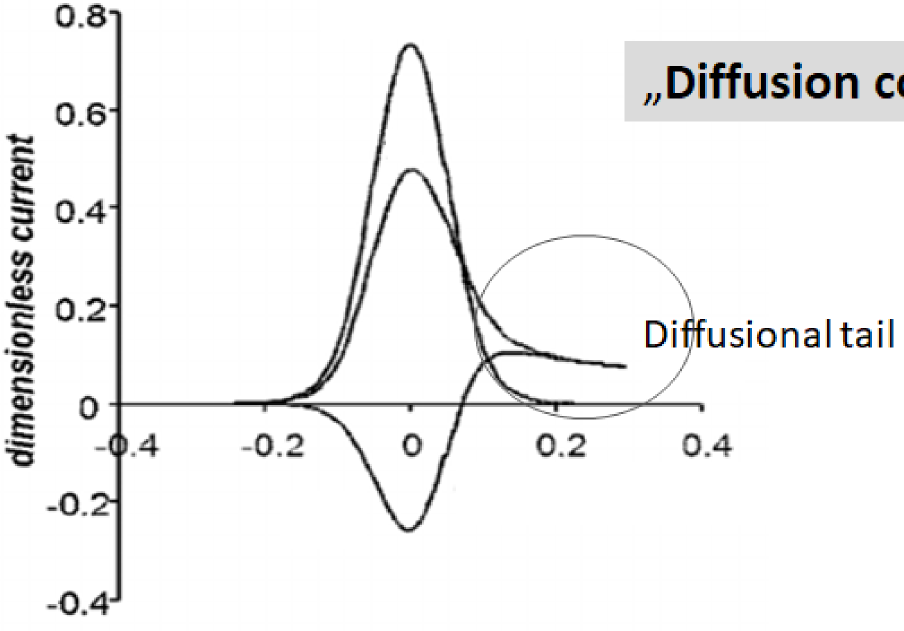


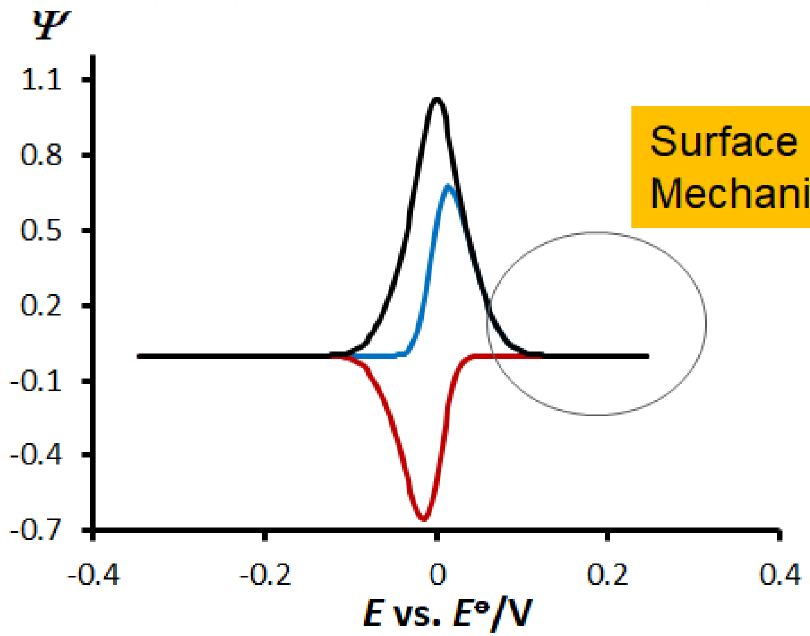
Features of the potential ramp in SWV and the manner for current measurements in SWV



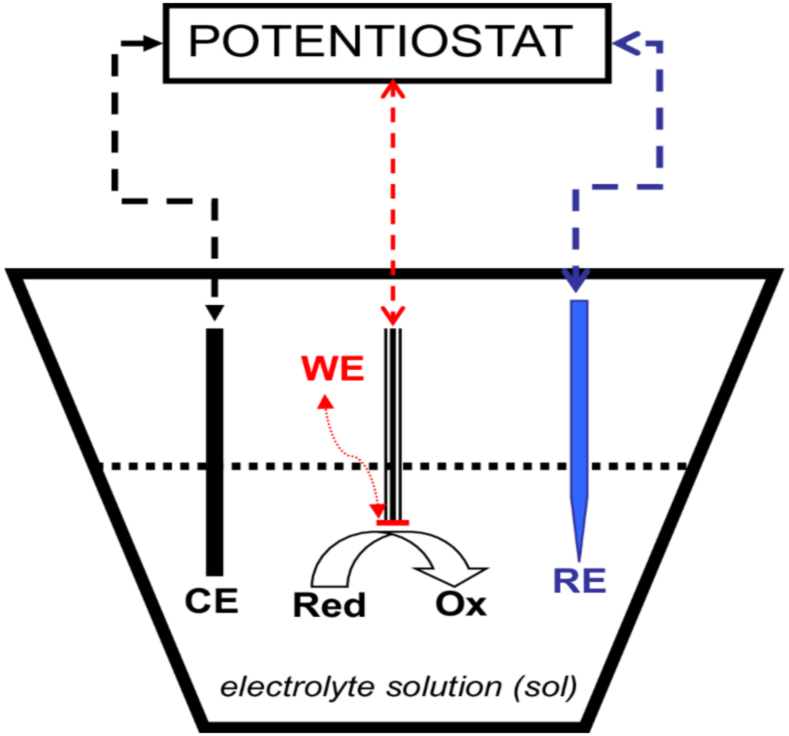

potential
time
(A)
potential
time
E_{sw}
ΔE
τ
(B)
dimensionless current
potential of the staircase ramp
$\Psi_{net} = \Psi_a - \Psi_c$
Ψ_a
Ψ_c
(C)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.4
-0.2
0
0.2
0.4



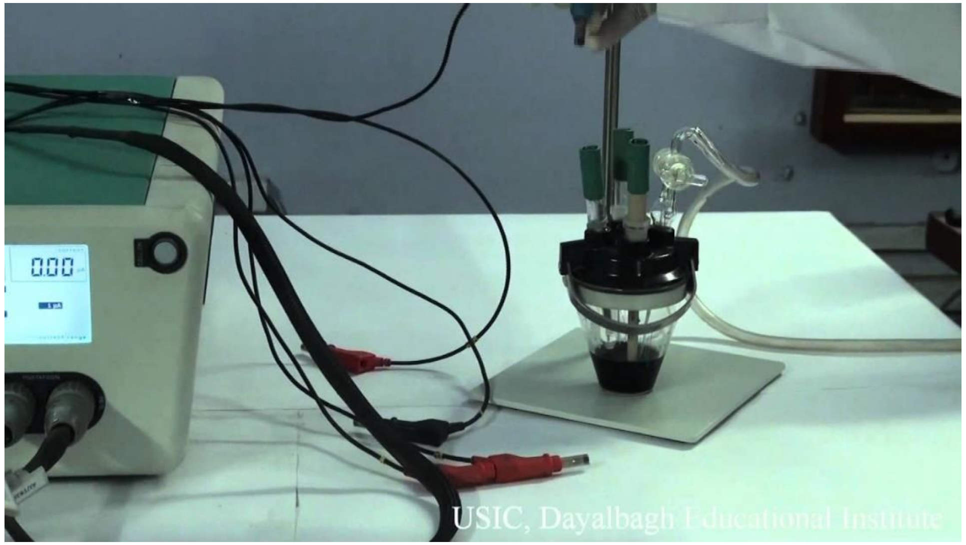
„Diffusion controlled reaction in SWV



Surface (adsorbed) electrode Mechanism in SWV



Potentiostat and working cell used in voltammetric experiments



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